4.5 PSP Cover Sheet (Attach to the front of each proposal)

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Distinguishing TOC Sources in the Delta Using Complex Chemical "Fingerprinting" of Organic Matter and Associated Contaminants

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State

Tax Status:

Non Profit

Tax Identification

Number:

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Executive Summary

Critical regional water research problems addressed

The broad class of substances that comprise aquatic natural organic matter (NOM), which includes "dissolved" and "particulate" organic matter (DOM and POM) are ubiquitous and known to strongly affect transport, degradation, bioavailability of both metal and organic pollutants, as well as nutrients. NOM plays a major role in other concerns such as trihalomethane formation in water treatment systems. It is now clear that the chemical structure of NOM are central to understanding water quality in terms of food webs and drinking water especially with CALFED's proposed ecosystem restoration projects.

While there has many of studies bulk NOM, very little is known about how its chemical structure is influenced by its source in the Delta. Without this information, there can be no scientifically rigorous basis for the management of aquatic NOM, including the nutrients and pollutants associated with it. By initiating a study of DOM and POM chemical structures, this research will generate information that is needed all agencies concerned with water quality, as well as by other researchers working in physical, chemical, and biological aspects of California's waterways. Bulk NOM may originate from peat soils, plankton and bacteria, various diffuse non point sources sources (Amy et. al, 1990; DWR, 1994-1995; Hoehn et. al, 1980; Krasner et. al 1996; Pomes et. al, 1999). However, the relative contribution of these various sources is not well understood. It is not known how CALFED's ecosystem restoration will affect the type and distribution of NOM and associated contaminants. This proposed study is an attempt to fill that data gap.

Results and benefits

This study will provide an initial look at the chemical structures of NOM present in major waterways of the Sacramento/San Joaquin Delta. The two analytical methods, pyrolysis-gas chromatography/mass spectrometry (pyro-GC/MS) and microanalysis X-ray fluorescence (MXRF), do not require a pre-selection of the desired analytes, so they can be operated as "fingerprinting" tools. In doing so, the study will also determine: (a) the applicability of these analytical techniques to the types of NOM structures found in Delta; (b) the extent to which these structures may vary by source and season; and thereby (c) provide a database for "fingerprinting" of aquatic NOM for determining sources of organic carbon and associated contaminants. The project will gather unprecedented high chemical content water quality data from important non point sources sources. Briefly, these are a residential wastewater treatment effluent, irrigation drains, delta open channels and CALFED restoration project. Utilizing adaptive management, data may be collected from other locations depending on resource availability.

However, both pyrolysis-GC/MS and MXRF go far beyond fingerprinting, because they also store detailed, potentially interpretable chemical information. The techniques are also relatively less labor intensive than other methods such as XAD resin extractions. The analytical data sets used for fingerprinting can be reprocessed later for targeted studies of aquatic NOM. For example, the data can be made to reveal: (a) lignin content to distinguish between predominantly terrestrial and aquatic NOM; (b) peptidic, phenolic, and bromine content to estimate propensity for disinfection by-products (DBPs) formation; (c) persistent, bioaccumulative, and toxic chemicals such as lead, polychlorinated biphenyls (PCBs) and poly-nuclear aromatic hydrocarbons (PAHs).

Summary of research approach

Our objective is to establish baseline information regarding the spatial and seasonal variability of aquatic NOM load and its key structural features in Sacramento/San Joaquin Delta. The Delta represents a good system for studying the roles of aquatic humic substances in multiuse waterways. For example, the Sacramento and San Joaquin Rivers are a primary drainage for water from agricultural, recreational, industrial, water impoundment, and flood control systems. Furthermore, most of these activities are highly seasonal and lie upstream of several municipal water intakes. Initially, five sampling sites and one replicate have been identified and they are described in the project section. We will utilize adaptive management approach to adjust the sampling plan after we have analyzed the initial data. However, data collected must provide information on possible dynamic and seasonal changes of the contaminants in the Delta area. One of the co-PI, Ngatia, who has worked in area of water resources management for more than 5 years, is an expert in field sampling techniques. In addition, Mr. Ngatia is familiar with and has many years' experience in analyzing the historical water quality data in the Delta. This historical data set will be used for water quality baseline determination in the Delta.

The proposed analytical method, pyro-GC/MS, has been used to examine the structures of NOM in air, soil, and sediments for over two decades. It has also been used widely for analysis of PCBs and PAHs from soil and sediment, and presence of lignin and cellulose structures. Recent advances in instrumentation has brought this technique to the point where it can be applied to a survey of aquatic NOM. The co-PIs Higashi and Fan have many years experience in using this technique. However, "fingerprinting" using this technique is a relatively new idea, and co-PI Higashi is currently funded by the California Resources Agency/Air Resources Board to test the method for identification of sources of fugitive dust (PM10). The proposed application to aquatic NOM is analogous to this air project.

The other proposed analytical method, MXRF, is often considered as a "total element analysis" tool. In air pollution studies, it is already established as a convenient way to obtain "signatures" of particulate matter (PM2.5 and PM10), and there is a growing application of this method in industry to monitor aqueous waste discharges. Its use for NOM studies is almost unknown, despite the fact that it can provide critical information to complement any organic analysis of NOM. Thus, the proposed application to aquatic NOM is unprecedented and will reveal information on mineral nutrients, halides, and metal contaminants that an organic chemical study on NOM alone cannot provide. Thus, it is complementary to the pyro-GC/MS analysis.

The primary objective of this project is to apply new and innovative techniques through field sampling and laboratory analyses to characterize the quantity and sources of the NOM and associated contaminants in the Delta. The fingerprint data sets collected through this project will generate a unique opportunity to draw an inference on the aquatic food. Prof. Geng, the PI of the project has been a faculty member of UCD since 1976. He is an expert in environmental modeling and assessment. Prof. Geng will use his expertise to model the data collected from the study.

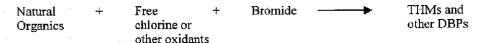
Project Description

Proposed Scope of Work

One of CALFED's six guiding principles to the solution of Delta problems is that any actions taken "result in no significant redirected impacts" (CALFED, February 1999). This means that CALFED-implemented solutions directed to solve one problem should not have significant negative impacts on other components of the Bay-Delta. In terms of water quality, CALFED's stated policy is to provide good quality water for all beneficial uses in the Delta.

Natural organic matter (NOM) is one of the important components in the aquatic ecosystem. However, NOM has varying impacts on different beneficial water uses. In the aquatic food web, energy is transferred through various trophic levels. The primary producers are at the lowest level and they may either convert the sun's energy via photosynthesis or use the energy stored in dissolved organic matter for their life processes. The primary producers are then consumed by the secondary consumers and so on up the food chain. Organic matter is therefore often considered to be a beneficial water quality constituent for aquatic organisms.

On the other hand, organic matter is a problem in drinking water. Organic matter and bromide ion negatively impact drinking water quality because they act as precursors of trihalomethanes (THMs) and other disinfection by-products (DBPs) during treatment to remove harmful microorganisms (DWR 1994-95, Krasner et al 1996, Paode et al. 1997, Pomes et al. 1999, Westerhoff et al 1998). DBPs are undesirable products in drinking water because they are suspected to be potential carcinogens in humans and are regulated by State and federal statutes. It is possible to partition the portion of DBPs formed from organic matter and bromide ion utilizing atomic mass units of organic matter and bromine. The chemical process leading to DBP formation is thought to be as follows:



However, the DBP formation is still not well understood. Currently, chlorine is the prevalent oxidant in drinking water treatment in the US. Proposed regulations to control harmful microorganisms especially *Giardia* and *Cryptosporidium* may require other more potent oxidants such as ozone. There is little scientific information on DBPs formed from those oxidants. However in general, source water quality is thought to play a major role in the amounts and types of DBPs formed.

In the past, California Department of Water Resources (DWR) drinking water investigations have mainly focused on bulk organic matter—the total organic matter in the aquatic system. High levels of NOM in Delta water have been attributed to releases from peat soils (DWR, 1993-97). A few studies have been attempted to characterize other sources of NOM such as algae using a regular fluorometer, spectrophotometer and fractionation using XAD resins with little success either because the methods are too time consuming or are not sensitive enough. A major obstacle in attempting to narrow down and characterize different sources of organic matter has been finding analytical methods that are precise enough to provide unique "fingerprints" and at the same time are reliable and utilize commercially available analytical tools. In the section on Chemical Fingerprinting Approach, we will list, by analogy with law enforcement agencies in real fingerprinting, the fundamental requirements for NOM source identification. These requirements exceed most analytical methods currently used

for NOM source identification. It will then list how the methods we are proposing meet all of these criteria.

Sampling rationale

This project will utilize pyro-GC/MS and MXRF, which in combination are very versatile in its ability to determine signatures of NOM. This "fingerprinting" approach will be used to characterize sources of organic matter and associated contaminants such as selenium, bromine and pesticides at the sampling sites described below. These sites have been selected because they represent relatively theoretically important sources of aquatic contaminants. The sites are a municipal water treatment effluent, source and tail end of an agricultural irrigation water drain, Delta ecosystem restoration projects (Figure 1). The sites are in CALFED's North Delta region. located in Yolo Basin Ecological Zone (CALFED February 1999). The watershed provides drinking water to over 400,000 people in Solano County as well as part of Napa County. The watershed has been documented to have the highest total organic carbon levels in the whole State Water Project (DWR 1998). Other desirable features considered in selecting this study area is the fact two of CALFED's major ecosystem restoration projects are in this area. Liberty Island will be restored by letting natural processes proceed with little human intervention (CALFED, personal communications). Prospect Island across the Deep Ship Channel form from Liberty Island is proposed to be restored by incorporating various man-made features. These activities are expected to be completed by the US Corp of Engineers by the year 2002. Results from Prospect Island will represent intensive restoration activities that can be compared with the natural restoration processes from Liberty Island.

Sampling sites selection rationale:

- Putah Creek near Winters and Ulatis Creek sites are a paired set. The Putah Creek near
 Winters will fingerprint source water from Lake Berryessa. Ulatis Creek will fingerprint
 this water after most of the water has been used for irrigation providing agricultural
 impacts.
- Old Alamo Creek near Elmira. This creek carries discharge from the Vacaville wastewater treatment plant. The site will provide fingerprint signatures associated with a residential wastewater treatment plant.
- Yolo Bypass near Liberty Island or Miner Slough at Prospect Island. The exact sites of
 these sampling stations will be determined later after field examination. The sites will
 fingerprint water quality in Delta channels feeding into the restoration project and inside
 the restoration project. If restoration on Prospect Island will not have been started by the
 time this research project is initiated, we will utilize adaptive management to select
 appropriate sampling sites at Liberty Island.
- Se impacts will be evaluated at San Joaquin River at Vernalis. This site has been sampled
 by various agencies including DWR for at least 10 years. Sampling will be coordinated
 with other agencies collecting data at the site.

For quality assurance purposes, one site will be randomly selected and duplicated during every sampling event following DWR's sampling protocols (DWR, August 1998). The sampling locations and frequencies are presented in Table 2 B. Sampling protocols will follow procedures in the Standard Methods, 19th Edition, DWR Sampling Manual for Environmental Sampling Programs (DWR 1994, 1995), US Geological Survey (1994).

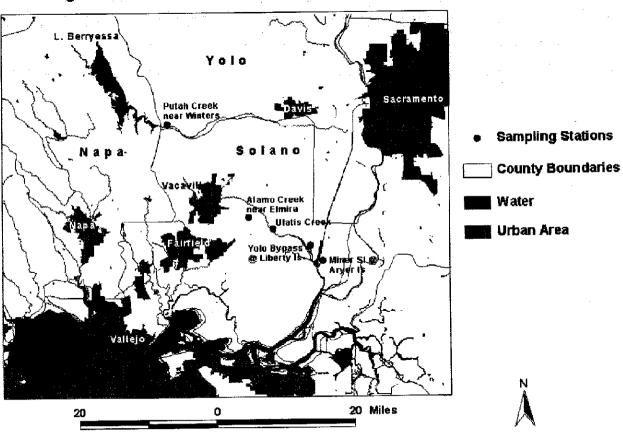


Figure 1 . North Delta Sampling Sites

The Chemical Fingerprinting Approach

Our strategy for distinguishing various sources of NOM takes advantage of the inherent complexity of aquatic system and its biogeochemistry based on factors such as land-use. For this application, the metaphor of "fingerprinting" has often been used. As with the real fingerprinting by lawenforcement agencies, the key features needed for identification are:

- 1) A material to analyze that exhibits a high dependence of its pattern on the particular source;
- 2) A highly complex pattern, so that (1) is actually an advantage rather than a hindrance;
- 3) Measurement technique that captures the complexity of pattern;
- 4) Minimal sample preparation;
- 5) Automated sample change, measurement, and data reduction;
- 6) Ability to analyze minute sample sizes and/or adverse samples;
- 7) Uses 100% off-the-shelf components for maximum uptime, multi-laboratory reproducibility, and ensured instrument improvements.

Clearly, this is a lot of ask of a technique. However, using either pyro-GC/MS or MXRF alone to analyze NOM (DOM and POM) meets, at once, ALL of the above requirements (1 through 7) for chemical fingerprinting:

- 1) As NOM is formed through biogeochemistry, it harbors the net organic matter from the particular biology, detritus, and chemistry at a given site;
- NOM is well known to have an extremely complex organic and organo-metallic chemical structure;
- 3) Pyro-GC/MS produces a very complex pattern that is structure-dependent, and MXRF also does to a lesser extent;
- 4) Both methods have minimal sample preparation. For pyro-GC/MS, POM is collected on quartz filters and directly analyzed, while DOM is freeze-dried and the powder is directly analyzed; for MXRF, POM is collected on teflon filters and directly analyzed, while DOM is spotted on a film and directly analyzed.
- 5) Both instruments in this study are equipped for auto-sample changing and analysis;
- 6) Pyro-GC/MS requires only micrograms or less of NOM, and is able to "pick out" sampling and storage contamination such as plasticizers, insect repellent, etc. MXRF for DOM requires only 0.020-0.050 ml of sample, while for POM requires a few mg.
- 7) Both instruments are 100% commercial products.
- 8) Used together, the two methods are complementary in what they measure.

Perhaps the most important aspect of pyro-GC/MS for CALFED's ecosystem restoration efforts is in the extremely high information content, such that this single analysis method can find utility in many other applications involving organic matter. For example, the propensity of aquatic humies to form trihalomethanes (THMs) in domestic water treatment systems appears to be linked to pyro-GC/MS analyzable humic structures such as polyhydroxyaromatics (Bruchet, et al., 1987; Bruchet, et al., 1990). While providing chemical fingerprinting, pyro-GC/MS can also analyze for some persistent, bioaccumulative, and toxic chemicals such as PAHs and PCBs. Our own work (Schultz et al., in press) demonstrates the capability of pyro-GC/MS to obtain DOM and POM fingerprinting and analysis of polynuclear aromatic hydromatters (PAHs) in the same analytical run.

Ecological/Biological Benefits

This project will provide a basis for evaluating whether CALFED's restoration projects have undesirable impacts on other parts of the Delta ecosystem. The project will also expand the tools needed in order to understand how the different components of the Delta ecosystem interact and therefore how to manage these different components. Although the study will be conducted in the Sacramento mainstem, the results obtained will be applicable to the entire Delta ecosystem.

Being able to "fingerprint" NOM in the aquatic ecosystem has many benefits. All Delta organisms operate at one food web level or another from the primary producers to the highest consumers. In order to understand the complex processes involved in the transfer of energy in these systems, it is important to understand the chemicals involved and the transformation of these chemicals from one food chain level to another. Organic matter is one of the most important of these natural chemicals. Organic matter is not only important as an energy source to aquatic organisms but it also plays a part in fate and transport of pesticides and other chemicals harmful to aquatic organisms. Organic matter may also aid in the transport of organisms such as Giardia and Cryptosporidium that are harmful to humans. In addition, organic matter may impair the physical quality of water through increases in turbidity.

It has been theorized that high turbidities and the consequent reduction in light transmission are the limiting factor in phytoplanktonic primary production rather than nutrients. Phytoplantonic growth is very important in improving the health of the aquatic food chain. Being able to fingerprint various DOC source contributions can help in determining what restoration alternatives best benefit endangered species such as Delta smelt, salmon, splittail etc.

This project will build on the historical information data that has been collected. The California Department of Water Resources has over 10 years of bulk organic matter concentrations at various locations in the Delta. Review of this data will give an overall view of the historical bulk distributions of organic matter as well as other elements such as selenium and bromide ion. This historical information has been used in this proposal in selecting sampling sites. The current research study will attempt to delineate and characterize possible sources of these chemicals thus adding useful information to the historical data.

Due to technical constraints, this phase of the project will attempt to characterize restoration, agricultural and residential wastewater sources of organic matter. Future phases will look at other sources such as urban runoff, concentrated animal facilities such as dairies. Another future effort will be to differentiate organic matter between algae and macrophytes.

This knowledge will be useful in food chain studies and drinking water protection through out the Delta. The knowledge will be useful in determining drinking water treatment facilities intakes. The project will not have any known impacts on third parties. It will not be in conflict with any existing agency obligations or mandates because currently water quality agencies are only required to monitor for bulk organic matter. These agencies are not funded to differentiate the different sources although it is knowledge that would help them in managing water quality for aquatic organisms as well as for drinking water purposes.

Among the chemicals of adverse impact in the Sacramento/San Joaquin River/Delta region, ecotoxicity of selenium compounds probably constitutes the most complex issue. There are large,

critical gaps in knowledge because of extensive biogeochemical transformation and bioaccumulation of the selenium element. This is exemplified by the unusually high body burden of Se found in a Bay/Delta invader species of clam (Asian clam, Potamocorbula amurensis) (Brown and Luoma, 1995) and resident sturgeon species (Kroll and Doroshov, 1991). The impact of a high Se body burden in sturgeon, particularly in its reproductive system, is unclear but may be of long-term consequence to sturgeon population since Se is well-known in causing reproductive failure such as tetratogenesis in bird and fish species (e.g. Ohlendorf et al., 1993; Lemly, 1993). Much less is known regarding the impact of Se pathway on other fish species of the Bay/Delta.

The observed high body content of Se is despite the low waterborne Se concentrations well below the EPA recommended 5 parts per billion limit – observed throughout the Bay/Delta. Such limits are many orders of magnitude below the detection limit of any direct bioassay, but deemed necessary since Se (as with other persistent, bioaccumulative, and toxic contaminants such as Hg and PCBs) ecotoxic impacts are transferred through the food chain. As a consequence, CALFED specifically called out the issue of Se and sturgeon as a top priority (CALFED PSP 1998), and thereafter funded research groups at Univ. of California-Davis (D. Hinton) and USGS-Menlo Park (S. Luoma).

Although these two CalFed projects address the upper, direct trophic transfer foodchain issues, a major knowledge gap remains in the entry and multiple re-entry points along the lower foodchain. Figure 1 and its legend illustrates that Se (as well as other persistent, bioaccumulative, toxic contaminants) does not proceed in a direct, trophic transfer up the food chain. The illustrated (Figure 2) residence time in the detrital material is not known and likely to be site-specific. Similarly, the bioavailability of the contaminants in the detritus is not known, but likely to be site-specific. This reflects a principal consensus opinion in the recent "Peer Consultation Workshop on Selenium Aquatic Toxicity and Bioaccumulation" held by the US Environmental Protection Agency.

Therefore, any change in water quality (resulting from different management practices) that significantly alters primary production and POM/DOM in the Bay/Delta, will most likely influence the Se foodchain transfer pathway and its ecological impact. This may well be illustrated in the observed changes in phytoplankton community (USGS pub), Asian clam invasion (Carlton et al., 1990), and Se bioaccumulation in Asian clam and sturgeon.

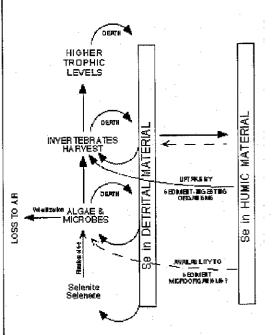
The importance of primary production and detritus is not limited to Se foodchain transfer, in that these water quality parameters have been implicated in the transport and bioavailability of many other trace metal and organic pollutants (e.g. Decho and Luoma, 1994), as well as drinking water quality. Yet, little is known about the relationship between source water quality and downstream biological impact. The proposed work on chemical fingerprinting of primary production and POM/DOM at relevant locations of the Bay/Delta is designed to probe the source water quality in detail. This information will then be integrated with ongoing CALFED-funded investigations on Se, trace metal, and pesticide transfer into high-risk fish species (in coordination with Drs. D. Hinton and S. Luoma), and with the long-term drinking water database established by California Department of Water Resources. Such integrated information will be valuable in guiding the long-term CALFED planning on water management in the Delta for beneficial uses including wetland/habitat restoration while ensuring drinking water safety.

Figure 2. Detrital organic matter is the biogeochemical "Grand Central Station" for accumulation of toxic elements up the foodchain.

For Se, their inorganic forms are biologically fixed by algae & microbes. However, Se – as well as other toxic elements such as As and Hg that are biologically fixed into organic forms – do not head directly up the foodchain. Since they are incorporated into organic matter, significant portions take a detour thru detritus (recently dead organic matter), then re-enter the foodchain at several trophic levels. Over longer periods, part of the detrital material converts to recalcitrant humic material, locking up the toxic elements until sediment-ingesting organisms reintroduce it to the foodchain.

Meanwhile, the unconsumed detrital material is continually breaking down to particulate organic matter (POM) and DOM, and transported downcurrent. The chemical nature of the POM and DOM determines their palatability (to re-enter the foodchain), and therefore affects ecological community structure as well as bioavailability of the toxic elements. The chemical structure is also the key for potential formation of disinfection byproducts. Therefore it is vital to begin establishing the chemical nature, toxic element load, and source fingerprints of POM and DOM through chemical fingerprinting.

Except for the initial "fixation" step, this organic matter storage reservoir scheme also applies to persistent, bioaccumulative, toxic organic chemicals such as PCBs and PAHs.



Technical Feasibility and Timing

NOM in water and sediments, which includes detritus, humics, and unavoidably microorganisms, is arguably the most chemically complex, which makes it the best target for source fingerprinting. We have reviewed the currently alternative methods for monitoring and characterizing NOM. The most widely utilized methods for analyzing bulk organic carbon are described in Standard Methods, 19th Edition (1995), but they can not distinguish any sources that make up the bulk organic carbon.

Several other techniques have been used to further characterize (but not necessarily to fingerprint) dissolved organic carbon (DOM) as summarized in Krasner, et al (June 1996). These other methods include XAD resin extraction, reverse osmosis, ultraviolet absorbance, fluorescence, carbon 13 nuclear magnetic resonance, and pyro-GCMS, but not the new MXRF technique proposed here, nor Fourier-transform infrared spectroscopy (FTIR) which is used very widely in NOM research elsewhere. XAD resins have been the most utilized in the past but suffer from their highly selective nature on organic carbon, plus they are also very time consuming and therefore relatively expensive.

In other fields, researchers in the 80's pursued chemical degradation of NOM under acid, oxidative, or reductive conditions, yielding apparently useful information regarding their structures (Hayes, 1991). However, this approach can also yield erroneous information as a result of extensive chemical modifications and rearrangements during the degradative processes; it also fails to provide information on secondary structures, which are essential for characterization of NOM (Hayes, 1991).

In contrast, the proposed pyro-GC/MS has been used widely in hypercomplex organic matter research (Hayes, 1991), including binding and transport of persistent, bioaccumulative, and toxic chemicals such as PAHs in our current research (Schultz et al., in press), and even microbe identification (c.f. Gutteridge, 1985; Helyer et al., 1993). It requires no sample preparation other than freeze-drying to remove water, and modern instruments require only very small amounts of organic matter (Higashi et al., 1994). For example, it obtains a complex fingerprint that is being used for identification of soils (Saiz-Jimenez, 1994) and sources of dust in our current research (Higashi et al., 1994) because the NOM pattern generated is dependent on land-use (e.g. agricultural crop).

Over the past decade, advances in techniques such as pyro-GCMS and FTIR have enabled researchers to compile more comprehensive structural information on NOM than was thought possible (Hayes, 1991). Pyro-GCMS has thus established itself as a cornerstone approach that is useful for the study of NOM (e.g. Haider and Schulten, 1985; Schnitzer and Schulten, 1992). For the most part, NOM researchers across many fields have ignored the metal and inorganic portions (often determined only as "ash"), but proposed our techniques of MXRF and other methods such as FTIR can obtain complex signatures from this unexplored area of NOM.

After having reviewed these various methods, we have come to the conclusion that pyro-GCMS and MXRF are the best methods currently available to "fingerprint" NOM. As stated earlier, we are already using pyro-GCMS to fingerprint NOM in fugitive dust in a project supported by the California Air Resources Board. Therefore, the likelihood of successfully accomplishing the tasks delineated in this proposal will be extremely high.

Monitoring and Data Collection Methodology

Biological/ecological objectives: The following are the hypotheses to be tested in this project (Table 2 A):

- 1. The chemical composition of natural organic matter in the Delta is primarily determined by the source of that organic matter.
- The pyrolysis-GC/MS and MXRF are sophisticated enough to distinguish the differences in organic matter.
- 3. Different sources of NOM will have different propensities to form disinfection byproducts.
- 4. Important contaminants in the Delta are associated with NOM.

Monitoring parameters and data collection approach: Sampling sites have been selected that will provide samples from different sources no point sources in the Delta. Surface water (and some sediment) samples will be collected at the following sites (Table 2 B, Appendix A):

- 1. Effluent from a residential water treatment plant (Old Alamo Creek site)
- 2. Irrigation drain return water (Putah South canal and Ulatis Creek)
- 3. CALFED restoration project (Liberty Island or Prospect Island). One station will sample channel water and the other inside the restoration project for comparison.
- 4. Using adaptive management, we will analyze limited amounts of samples for selenium from San Joaquin River at Vernalis.

Sampling will be conducted during wet and dry seasons for three years to detect any trends that are time dependent.

<u>Data Evaluation Approach</u>: Samples will be collected using techniques described in Standard Methods, 19th edition, DWR Sampling Manual for Environmental Monitoring Projects (1994) and USGS (1994). The sites will be mapped using GPS and geographical information systems (GIS). Data will be stored in database at Prof. Geng's laboratory and will be analyzed with standard statistical packages such Minitab, SAS and MatLab.

Historical data from agencies such as DWR will be reviewed for comparison. In addition, we will maintain coordination with CALFED's projects to help us in adjusting the project's objectives with new information. This will provide the basis for adaptive management of the project. Quarterly and annual reports to CALFED will be generated. These reports will be peer-reviewed by experts in water quality in the Delta. A final report with recommendations will be provided to CALFED. Journal reports will be prepared for submission to scientific journals. In addition, the investigators will be available for personal presentations at CALFED meetings. The timelines are presented as Table 5.

Table 2 A. Monitoring and Data Collection Methodology

Question/Hypothesis	Monitoring/Data	Data Evaluation	Comments, Data
	Collection Approach	Approach	Priority
What are the potential sources of	Literature review,	Detect any	Needed to confirm
NOM in the Delta?	analyze historical data	historical trends	candidate sampling
			stations
Is the chemical structure of	Collect samples from	Compute types of	Model TOC and
aquatic NOM in the Delta source	different sources.	NOM by source	contaminant
dependent?	Fingerprint with p-		relationships with
Is there relationships between	GC/MS and MXRF.		DBP formation.;
NOM and important	Also analyze with		evaluate potentisi
contaminants such as Se, Hg?	traditional standard		impacts to
	methods for DBPs	<u> </u>	foodwebs
Is the NOM from restoration	Use adaptive	Compare NOM	Model potential
projects different from that from	management for short	signatures from	effects of
other Delta sources?	term intensified sampling	restoration project	restoration projects
	of other restoration	against other	on TOC
•	projects	sources	

Table 2 B. Data collection	and analyses		<u> </u>
Sampling Location	Parameter	Frequency	Comments
	Field measurements:		
Old Alamo Creek near	<u></u>		
Elmira	Surface EC, Temp, DO, pH,	Monthly	Winter
	fluorescence*		monthly
Putah South Creek		Modify sampling	only collect
Canal near Berryessa	Pyro-GCMS analyses	program as needed	samples during
	TOC, DOC (Filtered in field)	Using adaptive	flood events
Ulatis Creek at Highway		management	
113	Standard Methods analyses		
•	Bromide ion, chloride ion,		May use
Channel inlet into	Selenium, TOC, Alkalinity, DOC		adaptive
Prospect Island	(Filtered in Field), UVA-254nm;		management to
_	Reactivity THMFP, Volatile and		sample Liberty
Drainage Canal from	Suspended Solids		Island
Prospect Island			
Duplicate: Randomly	Duplicate for quality assurance		,
selected	,		
$\varphi_{i,j} = \varphi_{i,j} \circ \varphi_{i$			

^{*}EC: Electrical conductivity; Temp Temperature; DO: Dissolved oxygen UVA: Ultraviolet absorbance at 254nm, TTMFP: Total trihalomethane formation potential

Table 2 C. Sampling sites characteristics

Table 2 C. Gamping sites charac	DOTTS CO.	
Sampling Location	Rationale for selection	Comments
Old Alamo Creek near Elmira	Collect signature of effluent from a residential water treatment plant	Using adaptive management, may sample
Putah South Creek Canal near Berryessa	Collect signatures of water before irrigation	different sites
Ulatis Creek at Highway 113	Collect signatures of water after irrigation	
Channel inlet into Prospect Island	Collect quality attributes before water Circulates through restoration project	
Drainage Canal from Prospect Island	Collect signatures after water circulates through restoration project	
Duplicate: Randomly selected	Duplicate for quality assurance	

Local Involvement

We have informed David Okita (the Solano County Water Agency), John B. Meek (San Joaquin county), and Larry Clement (Yolo County), that we have submitted a proposal to CALFED for funding considerations in conducting water quality related research in their respective counties (letters are attached). We have also asked their considerations for possible coordination with the water projects that are presently conducted in their regions. Letters are included as attachments.

We believe, if our project is funded, the fingerprinting data that we will generate and the interpretative results that we will provide, can be used by those local governments to enhance their decision making ability on issues related to water quality and ecological risk management.

In addition, we will work with the California Department of Fish and Game, Department of Water Resources and CALFED to make sure the information we obtain will be timely distributed and fully utilized to serve their respective agency mandates and goals.

Cost

Budget figures are presented in Table 3 and 4. The breakdown of budget by tasks is as follows We have budgeted \$10,000 for the first year (and plus 5% increase per year for the second and the third year) for project monitoring costs. This amount of money will be used to cover part of the costs to manage the detailed activities of the project such as inspection of work in progress, validation of costs, and preparation of periodic reporting requirements. It should be noted that Dr. Shu Geng, the PI is having the primary responsibility of monitoring the overall performance of the project. Since Dr. Geng's salary is paid by the university, therefore, the budgeted monitoring and management costs do not reflect the total commitment of this proposed research. The accounting and auditing task of the project will be assumed by the Administration Office of the PI's department, as part of the cost sharing contribution by the university.

The University of California requires a different overhead rate for State and Federal projects. The State rate is less than 25%. The Federal rate is 44.5%, which is a standard overhead rate for all university systems in California.

The start/completion dates of each of the proposed tasks are shown in Table 5. We have breakdown the main tasks into 5 categories and within each category there area number sub-tasks to make sure that each of the tasks is well defined and the responsibilities are clearly designated among the investigators. We are familiar with and are totally committed to the quality assurance/quality control concept in environmental monitoring.

Cost Sharing

The total cost sharing contribution of the University of California is \$143,000. An itemized list of the cost sharing contributions from the PI's and co-PI's are shown below,

1. Personnel: Total UCD cost sharing contribution of \$62,000 per year for 3 years.

Shu Geng's Salary contribution (35%) \$60,000 per year Accountants' time in the Administration Office in the Department of Agronomy and Range Science, University of California at Davis (5%): \$2,500 per year.

- 2. Use Existing Equipment: Total UCD cost sharing contribution of \$81,000 for 3 years
 - (i) Computers: 2 workstations in the Dr. Geng's laboratory will be designated to the project. The cost is \$3,000 per computer, or a total \$6,000 towards cost sharing.
 - (ii) Analytical instruments:

 The cost sharing will be 25% of the instruments cost, which are listed below,
 Three gas chromatography mass spectrometers (GCMS), each costs \$80,000
 Microanalysis X-ray fluorescence (MXRF) at a cost of \$80,000
 HPLC at \$100,000
 Two scanning fluorescence spectrophotometer at \$40,000

Applicant Qualifications

Dr. Shu Geng is a professor in the Department of Agronomy & Range Science and is the Principal Investigator of the East Asia Center on Population, Resources and Welfare of the University of California, Davis. Recently he has worked with the Pacific Basin Study Center, published the book, "the Sustainable Development of Rice as a Primary Food" and is working with the Faculty of the Kyoto University as an editor to publish the Proceedings of the Symposium, "World Food Security and Crop Production Technologies for Tomorrow". Dr. Geng's research has been in the area of sustainable agricultural systems and environmental impact assessment. More recently his research has focused on evaluating global climate change impact on agricultural production and on GIS modeling of underground water quality in California. He is a member of Sigma Xi; Pi Mu Epsilon; American Society of Agronomy; Crop Science Society of America, American Association for the Advancement of Science. He is an elected Fellow of the American Association for the Advancement of Science and a fellow of the American Society of Agronomy. As a faculty member at UCD for 23 years, he has authored or co-authored more than 100 refereed papers and is a frequent speaker in international symposiums. Three recent publications (with collaborators) are shown below, "Multiscale Influences of Gophers on Alfalfa Yield and Quality Field Crops Research, V49 (2-3):159-168"; "Assessing Groundwater Nitrate Contamination for Resource and Landscape Management. AMBIO 27: 170-174"; "Quantifying the agricultural Landscape and Assessing Spatio-temporal Paterns of Precipitation and Groundwater Use. Landscape Ecology 13: 37-53". He can be contacted at Tel: 916-752-6939, Fax: 916-752-4361, E-mail: sgeng@ucdavis.edu. Shu Geng will serve as the PI of the project. He will be responsible for the overall performance and the progress of the tasks of the project. Specifically, he will be responsible for environmental modeling and impact assessment.

Dr. Teresa W-M. Fan is an associate research professor in the Department of Land, Air and Water Resources, University of California, Davis. Her research interest has been in the broad area of environmental biochemistry ranging from plant stress biochemistry and Se biogeochemistry in relation to in situ bioremediation, to mechanisms of aquatic ecotoxicity of agricultural and industrial discharges. Along CalFed's interest, she has been working on salinity and toxic metals stress on the Asian clam, Potamocorbula amurensis, in the Delta/San Pablo Bay, as well as the tradeoffs between algal phytoremediation and ecotoxic risk of selenium in San Joaquin Valley's evaporation ponds. She has served on the 9-member EPA Peer Consultation Workshop on Selenium Aquatic Toxicity and Bioaccumulation (March 1998) which concluded that selenium organic forms and foodchain biochemistry - not total Se - should be the target of ecotoxic investigations and bioremediation goal. Most recently, she was one of the authors of the Central Valley Drainage Implementation Program's comprehensive report on Discharge to the San Joaquin River. Example of recent authored and coauthored publications: Biotransformations of Selenium Oxyanion by Filamentous Cyanophyte-Dominated Mat Cultured from Agricultural Drainage Waters. Lane, Environmental Science and Technology 32, 3185-3193 (1998); Biochemical Fate of Selenium in Microphytes: Natural Bioremediation by Volatilization and Sedimentation in Aquatic Environments, In: Environmental Chemistry of Selenium, W.T. Frankenberger and R.A. Engberg, eds., Marcel Dekker, Inc., New York, pp. 545-563 (1998); Synthesis and structure characterization of selenium metabolites. Analyst 123(5), 875-884 (1998); Characterization of Two Humic Acid Fractions from a Calcareous Vermiculitic Soil: Implications for the Humification Process. Geoderma, 65, 195-208 (1995).

Dr. Richard M. Higashi is an assistant research professor in the Crocker Nuclear Laboratory, University of California, Davis. He has worked in broad areas of environmental chemistry, ranging from toxicity identification in complex effluents such as pulpmill and oil production discharges, to DOE waste contamination remediation, to agricultural water, soil, and sediment problems of the Central Valley and San Francisco Bay/Delta, as well as air pollution (PM10 and ozone) research in the Central Valley and Sierra Nevada Range. The chemistry of humics and other organic matter plays a central role in ALL of these research areas, and he is currently engaged in organic matter chemistry investigations in relation to selenium ecotoxic remediation in evaporation ponds of the SJV. Example of relevant publications: Sorption-desorption behavior of phenanthrene elucidated by pyrolysis-GCMS studies of soil organic matter. Environmental Toxicology and Chemistry, in press; Association of desferrioxamine with humic substances and their interaction with cadmium(II) as studied by pyrolysis gas chromatography mass spectrometry and nuclear magnetic resonance spectroscopy. Analyst 123(5), 911-918 (1998); Selenium Biotransformations by a Euryhaline Microalga Isolated from a Saline Evaporation Pond. Environmental Science and Technology, 31, 569-576 (1997); Microphytes-Mediated Selenium Biogeochemistry and Its Role in In Situ Selenium Bioremediation. In: Phytoremediation, N. Terry, ed., Ann Arbor Press, in press.

Mr. Murage Ngatia (Co-Investigator) is an environmental specialist with California Department of Water Resources. He has been working with DWR since 1994 as a water quality specialist. He has been in charge of many projects investigating water quality in the Sacramento/San Joaquin Delta. He has co-authored several DWR's water quality reports and quality assurance documents. He has also been a coordinator and instructor of the Department's quality assurance/quality control classes. Recent publications: Fong, Sid et al, May 1998, Bryte Chemical Laboratory Quality Assurance Manual. Quality Assurance Technical Document 8. California Department of Water Resources; Ngatia, Murage and Barry Gump, September 1997. Quality Assurance Guidelines for Analytical Laboratories. Quality Assurance Technical Document 1. California Department of Water Resources; Ngatia, Murage, June 1997. Compilation of Federal and State Drinking Water Standards and Criteria. Quality Assurance Technical Document 3. California Department of Water Resources; Tom, Raymond et al, December 1997. Quality Assurance Management Plan for Environmental Monitoring Programs. Quality Assurance Technical Document 5. California Department of Water Resources; Tom Raymond et al, August 1995. Municipal Water Quality Investigations Program, Annual Report, Water Year 1995-96. California Department of Water Resources.

Table 3. Total Budget (CALFED funds only)

Task	Direct Labor Hours	Direct Salary and benefits	Service Contracts	Material & Acquisition Costs	Miscellaneous & other Direct Costs	Overhead and Indirect Costs	Total Costs
Year 1							
Field Sampling	2063	103194	N/A	N/A	4000	15479	\$122,673
Pyro-GCMS fingerprinting	468	35345	N/A	26000	10000	5302	\$76,647
Standard Methods analysis	N/A	N/A	22320	N/A	N/A	N/A	\$22,320
Data analyses and modeling	983	49156	N/A	14000	3000	7373	\$73,529
Project monitoring	N/A		N/A	N/A	10000	N/A	\$10,000
Subtotal	I				.t		\$305,169
Year 2							
Field Sampling	2167	108353	N/A	N/A	4200	16253	\$128,806
yro-GCMS fingerprinting	742	37112	N/A	N/A	10500	2066	\$49,678
Standard Methods analysis	468	N/A	23436	N/A	N/A	N/A	\$23,436
Data analyses and modeling	1032	51613	N/A	N/A	3150	2896	\$57,659
Project monitoring	210	N/A	N/A	N/A	10500	N/A	\$10,500
Subtotal	*.!-						\$270,079
Year 3							
Field Sampling	2275	113771	N/A	N/A	4409	11377	\$129,557
yro-GCMS fingerprinting	779	38968	N/A.	N/A	11025	3896	\$53,889
Standard Methods analysis	492	24607	N/A	N/A	: N/A	N/A	\$24,607
Data analyses and modeling	1149	57484	N/A	N/A	3307	5748	\$66,539
roject monitoring	220	11025	N/A	N/A	N/A	N/A	\$11,025
Subtotal							\$285,617
Total							\$860,865

Table 4. Quarterly budget

Year-l Task	Quarterly Budget Oct-Dec 99	Quarterly Budget Jan-Mar 00	Quarterly Budget Apr-Jun 00	Quarterly Budget Jul - Sep 00	Total Budget
1. Field Sampling	30668	30668	30668	30668	122672
2. Pyro-GCMS fingerprinting	19162	19162	19162	19162	76648
3. Standard Method analysis	5580	5580	5580	5580	22320
4. Data analysis and modeling	18382	18382	18382	18382	73528
5. Project monitoring	2500	2500	2500	2500	10000
Total	76292	76292	76292	76292	305168
Ycar-2 Task	Quarterly Budget Oct-Dec 00	Quarterly Budget Jan-Mar 01	Quarterly Budget Apr-Jun 01	Quarterly Budget Jul - Sep 01	Total Budget
1. Field Sampling	32201	32202	32202	32202	128807
2. Pyro-GCMS fingerprinting	12419	12419	12419	12419	49676
3. Standard Method analysis	5859	5859	5859	5859	23436
4. Data analysis and modeling	14415	14415	14415	14415	57660
5. Project monitoring	2625	2625	2625	2625	10500
Total .	67519	67520	67520	67520	270079
Year-3 Task	Quarterly Budget Oct-Dec 01	Quarterly Budget Jan-Mar 02	Quarterly Budget Apr-Jun 02	Quarterly Budget Jul - Sep 02	Total Budget
1. Field Sampling	32389	32389	32389	32389	129556
2. Pyro-GCMS fingerprinting	13473	13472	13472	13472	53889
3. Standard Method analysis	6152	6152	6152	6152	24608
4. Data analysis and modeling	16635	16635	16635	16635	66540
5. Project monitoring	2756	2756	2756	2756	11024
Total	71405	71404	71404	71404	285617

Table 5. Project Timelines

TASKS

1. Field Sampling

Site evaluation
Sampling procedure verification
Baseline information construction
Monitoring data collection
Adaptive management review and implementation

(a) Pyrolysis-GCMS and MXRF "fingerprinting" analysis
 Methodology and procedure verification
 Sample analyses
 Chromatographic conversions
 Adaptive management review

2. (b) Standard Methods chemical analyses

Disinfection byproducts chemical analysis using reactivity test Adaptive management review and implementation

3. Data analyses

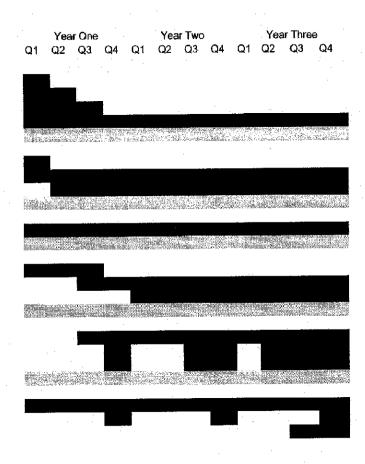
Historical data review and summarization Chromatograph data interpretations Station by station water quality comparisons Adaptive management review and implementation

4. Model construction and environmental impact assessment

Ecological impact model construction
Aquatic food web impact analyses
Disinfection byproducts model analyses
Adaptive management review and implementation

5. Project Monitoring and reporting

Quarterly and annual progress reports Annual presentation to the public or CALFED Final report and journal paper preparation



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Application Construc		Preapplication Construction	4. DATE RECEIVED B	Y FEDERAL AGENCY	Federal Identifier
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	Catalog of	Estimated Unobliga	A BUIDGE SUMME ted Funds	New or Revised Bud	lget	
Grant Program Function or Activity (a)	Federal Domestic Assistance Number (b)	Federal (c)	Non-Federal (d)	Federal (e)	Non-Federal (f)	Total (g)
Field sampling	N/A	N/A	N/A	\$153,115	N/A	\$153,115
2. Chemical analysis	N/A	N/A	N/A	108087	N/A	\$108,087
3. Data analysis and modelin	g N/A	N/A	N/A	88031	N/A	\$88,031
4. Project monitoring	N/A	N/A	N/A	10000	N/A	\$10,000
5. Total	N/A	N/A	N/A	\$359,233	N/A	\$359,233
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6. Object Class Categories			GRANT PROGRAM,	FUNCTION ACTIVIT	Υ	
d. Object Glace Gategories		1	2	3	4	Total (5)
a. Personnel		\$88,200	\$27,727	\$39,450	N/A	\$155,387
b. Fringe Benefits	-	14994	4714	6707	N/A	\$26,415
c. Travel		N/A	2000	4335	N/A	\$6,335
d. Equipment		N/A	26000	14000	. N/A	\$40,000
e. Supplies		1500	10000	3000	N/A	\$14,500
f. Contractual	·	N/A	22320	. N/A	N/A	\$22,320
g. Construction		N/A	N/A	N/A	N/A	N/A
n. Other	·	2500	N/A	N/A	\$ 10,000	\$12,500
Total Direct Charges	(sum of 6a-6h)	\$107,194	\$92,761	\$67,492	N/A	\$267,447
j. Indirect Charges		\$45,921	\$15,325	20540	N/A	\$81,786
k. TOTALS (sum of 6i a	nd 6j)	\$153,115	\$108,086	\$88,032	\$ 10,000	\$359,233
	reja tir beber					
7. Program Income	The same of the sa	\$ N/A	\$ N/A	\$ N/A	\$ N/A	\$ N/A

BUDGET INFOR	RMATION - Non-Construc	tion Programs:			e o nome de la compansión	
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12. TOTAL (sum of lines 13 and 14)		\$	\$	 \$	\$	
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13. Federal	Total for 1st year	1st Quarter		3rd Quarter	4th Quarter	
	\$359,233	\$119,808	\$67,255	\$67,255	\$67,25	
14. Non Federal	N/A	N/A		N/A	N/A	
15. TOTALS (sum of lines 13 and 14)	\$359,233	\$119,808	\$67,255	\$67,255	\$ 67,25	
LE THE PROPERTY SECTION ES BUDGET, ESTIMATES OF	IZEOEKA LEUNDIS NIEED				Tara da la	
(a) Grant Program		FUTURE FUNDING PERIODS (Years)				
	(b) First	(c) Second	(d) Third	(e) Fourth		
16. Field sampling	\$160,696	\$168,730		\$		
17. Chemical analysis	87126	91480				
18. Data analysis and modeling	77582	81461				
19. Project monitoring	10500	11025		-		
20. TOTAL (sum of lines 15-19)	\$335,904	\$352,696				
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21. Direct Charges	22. Indirect Cha	rges: As negotia	ted			
23. Remarks						

Standard Form 424A (Rev. 4-92) Prescribed by OMB Circular A-102

Appendix-A: Literature Cited

- Amy, G.L. et al. 1990. Evaluation of THM precursor contributions from agricultural drains. AWWA Journal.
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- Bruchet, A., Rousseau, C., Mallevialle, J. (1990) Pyrolysis-GC-MS for investigating high-molecular weight THM precursors and other refractory organics. J. Am. Waste Water Assoc. 66-74.
- Bruchet, A., Anselme, C., Marsigny, O., Mallevialle, J. 1987) THM formation potential and organic content: a new analytical approach. Aqua 2: 102-109.

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APPENDIX -B: LETTERS TO LOCAL AGENCIES

UNIVERSITY OF CALIFORNIA, DAVIS



95616-8515

SANTA BARBARA • SANTA CRUZ

DAVIS, CALIFORNIA

SHU GENG, PROFESSOR DEPARTMENT OF AGRONOMY AND RANGE SCIENCE COLLEGE OF AGRICULTURAL AND ENVIRONMENTAL SCIENCES TEL. (330) 752-6939 FAX: (530) 752-4361 EMAIL: ageng@wodnvis.edu

> April 13, 1999 David Okita Solano County Water Agency 508 Elmira Rd Vacaville 95687

Dear Mr. Okita,

We are submitting a proposal to CALFED to study water quality related issues in Barker Slough Watershed, Solano County. If the proposal is funded, we would like to work with you and to coordinate with your other projects in the county to improve water quality in the region. Thank you for your attention and we sincerely hope we will have the opportunity to work with you in future.

Sincerely,

Shu Geng Professor

CC: Teresa Fan, Rick Higashi, Murage Ngatia

BERKELEY . DAVIS . IRVINE . LOS ANGELES . RIVERSIDE . SAN DIEGO . SAN FRANCISCO



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April 13, 1999

John B. Meek, Jr. 1222 Monaco Ct., Suite 23 Stockton, CA 95207-6742

Dear Mr. Meek,

We are submitting a proposal to CALFED to study water quality related issues in San Joaquin County. If the proposal is funded, we would like to work with you and to coordinate with your other projects in the county to improve water quality in the region. Thank you for your attention and we sincerely hope we will have the opportunity to work with you in future.

Sincerely,

Shu Geng Professor

CC: Teresa Fan, Rick Higashi, Murage Ngatia

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TEL: (330) 752-6939
FAX: (530) 752-4361
EMAIL: sgeng@wodavis.sdu

April 13, 1999

Larry Clement 221 W Court #5 Woodland, CA 95695

Dear Mr. Clement,

We are submitting a proposal to CALFED to study water quality related issues in San Joaquin County. If the proposal is funded, we would like to work with you and to coordinate with your other projects in the county to improve water quality in the region. Thank you for your attention and we sincerely hope we will have the opportunity to work with you in future.

Sincerely,

Shu Geng

Shubery

Professor

CC: Teresa Fan, Rick Higashi, Murage Ngatia